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(54) Thermal swing adsorption process for the removal of dinitrogen oxide, hydrocarbons and other trace impurities from air

(57) The present invention provides a temperature swing adsorption process for purifying atmospheric air prior to its separation by cryogenic distillation. The process utilizes three adsorbent layers, the first primarily removes water and may be activated alumina; the second primarily removes CO₂ and may be NaLSX; and the third layer is designed to remove gas components such as N₂O and hydrocarbons which are displaced from the second layer. It has been found that CaX type adsorbents provide the removal of N₂O and hydrocarbons in the third layer.

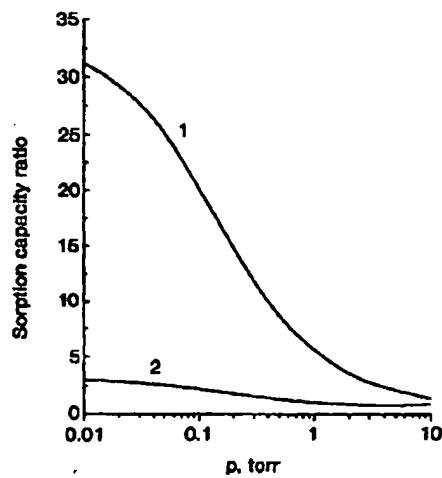


FIG. 1

Description

[0001] The present invention is directed to a thermal (temperature) swing adsorption process, TSA, for removal of trace impurities such as dinitrogen oxide, N₂O, (nitrous oxide) and hydrocarbons from air, and to the adsorbent composition for this process. In particular, the present invention is directed to a TSA process for use in prepurification units, PPUs, prior to cryogenic separation of oxygen and nitrogen from air.

[0002] Upstream of cryogenic separation of oxygen and nitrogen from air, various trace impurities must be removed to avoid formation of solids in the heat exchanger equipment and resultant high pressure and safety issues in the cryogenic process. The most obvious trace air impurities that must be removed include carbon dioxide, CO₂, and water, H₂O. There are many references which disclose the use of pressure swing adsorption, PSA, and TSA to remove these types of impurities from air in pre-purification units upstream of cryogenic separation of oxygen and nitrogen from air. For example, see DE-A-3 045,451; US-A- 4,711,645; US-A- 4,249,915; US-A- 5,232,474; Great Britain-A- 1,586,961 and EP-A- 0 449 576. In addition, EP-A- 0 862 938 discloses a PSA process for the removal of nitrogen oxides in addition to carbon dioxide and water from gases prior to cryogenic processing in air separation units, ASU. Finally, EP-A-0 930 089 discloses a TSA process for removal of CO₂ from air using various zeolite adsorbents.

[0003] The importance of the removal of nitrogen oxides, particularly nitrous oxide, from air prior to entering into a cryogenic air separation plant has recently been acknowledged. The removal of N₂O is particularly important because of its increase in concentration in the atmosphere. It is well known that N₂O is a greenhouse gas and the concentration of N₂O in the atmosphere (currently about 0.3 ppm) has been increasing steadily (by about 0.2 to 0.3% annually). This increase is mainly caused by anthropogenic activities as well as by emissions from various chemical processes. An excess of N₂O in cryogenic air separation units may lead to tube plugging in heat exchangers and contamination of the products. The fact that N₂O is very stable in air and its atmospheric lifetime comprises of about 150 years makes the removal of N₂O in an air pre-purification unit absolutely essential in both present time and the future. It is envisaged that in the future the removal of N₂O will become as important as the removal of water and CO₂. As the concentration of N₂O in air increases further, the current regime of PPU processes will become inadequate because N₂O cannot be removed easily by existing PPU processes. Accordingly, there is a clear need to develop an improved adsorption process suitable for use in PPU units to remove not only water and CO₂ but also the trace amounts of nitrogen oxides, in particular N₂O, which are present in the air being sent to the cryogenic separation unit. In addition, great care should be

taken for the removal of hydrocarbons, such as low-molecular weight hydrocarbon gases, methane, ethane, propane, n-butane, iso-butane as well as any non-saturated species, such as acetylene, ethylene, propylene, the n-butylene isomers and the iso-butylene isomers, from air in PPU processes. It is also important that both hydrocarbons and plugging components such as N₂O and CO₂ be simultaneously removed in the air pre-purification process. Deposits of plugging components may create an opportunity for hydrocarbons to collect and concentrate in these deposits.

[0004] Typically, the feed to a cryogenic air separation unit comprises atmospheric air containing H₂O vapor, CO₂ and trace impurities including N₂O, acetylene, propane and other hydrocarbons. This feed is normally passed through a TSA pre-purification unit (PPU) to remove the H₂O and CO₂. Known TSA-PPU designs while suitable for the removal of H₂O and CO₂ from air are not adequate for the complete removal of the trace impurities such as various nitrogen oxides and/or hydrocarbons. The process of the present invention is directed to a novel adsorbent arrangement for use in a TSA-PPU which not only removes H₂O and CO₂ from the air feed but also removes substantially all the nitrogen oxides, in particular N₂O, and hydrocarbons, in particular C₂H₄, from the air feed prior to entry of the air feed into the ASU for the separation of N₂ and O₂.

[0005] It is an object of the present invention to provide a novel temperature swing adsorption process which removes trace nitrogen oxides, impurities especially nitrous oxide, from air.

[0006] It is a further object of the present invention to provide a novel temperature swing adsorption process which removes trace hydrocarbons from air upstream of entering into a cryogenic distillation unit for separation of oxygen and nitrogen from air.

[0007] Additional objectives and advantages of the invention will be set forth in part at the end of the description which follows and in part will be obvious from the description or may be learned by practice of the invention. The objectives and advantages of the invention may be realized and attained by means of the processes and combinations particularly pointed out in the appended claims.

[0008] To achieve the foregoing objects and in accordance with the purpose of the present invention as embodied and described herein, the gas separation process of the present invention comprises passing a gas stream containing impurities comprising water, carbon dioxide, dinitrogen oxide (nitrous oxide), and hydrocarbons into a temperature swing adsorption unit wherein the gas stream is passed through a first adsorbent capable of removing the water from a gas stream, then through a second adsorbent comprising a sodium X-type zeolite wherein the Si/Al elemental ratio of the zeolitic phase ranges between from about 0.9 to 1.3 to remove the CO₂ impurity from the gas stream, and then passing the gas stream through a third adsorb-

ent comprising a X-type zeolite having a Si/Al elemental ratio of the zeolitic phase, ranging from about 0.9 to 1.3, whose exchangeable cations on an equivalent basis include about 0 to about 100 % calcium ions, and about 100 to about 0 % other ions, the other ions being selected from the group consisting of Group IA ions such as lithium, sodium and potassium, from Group IIA ions other than calcium, from Group IB ions other than gold, from Group IIB ions other than mercury, and from ions of the lanthanides, and mixtures of these, to remove the dinitrogen oxide and hydrocarbon impurities from the gas stream.

[0009] In a preferred embodiment of the present invention, the TSA process is provided in an air pre-purification unit upstream of entry of the gas stream into the cryogenic air separation process.

[0010] In a further preferred embodiment of the present invention, the first adsorbent layer is activated alumina.

[0011] In a still further preferred embodiment of the present invention, the second adsorbent layer is a sodium Low-Silicon-X zeolite (NaLSX zeolite), wherein the Si/Al elemental ratio of the zeolitic phase ranges between 0.9 and 1.15, more preferably between 0.95 and 1.05.

[0012] In a still further preferred embodiment of the present invention, the third adsorbent layer is a LSX zeolite wherein the Si/Al elemental ratio of the zeolitic phase ranges between 0.9 and 1.15, and whose exchangeable cations on an equivalent basis include about 60 to about 100 % calcium ions, and about 40 to about 0 % other ions, the other ions being selected from the group consisting of Group IA ions such as lithium, sodium and potassium, from Group IIA ions other than calcium, from Group IB ions other than gold, from Group IIB ions other than mercury, and from ions of the lanthanides, and mixtures of these.

[0013] In a most preferred embodiment of the present invention both the second and the third adsorbent layers comprise the sodium cation exchanged form of LSX type and the calcium cation exchanged form of the X-type zeolite, respectively, wherein the Si/Al elemental ratio of the zeolitic phases ranges from 0.95 to 1.05, and the cation composition of the third adsorbent comprises from about 95 to about 100 % of calcium ions and about 5 to about 0 % of cations being selected from the group consisting of Group IA such as lithium, sodium and potassium, from Group IIA ions other than calcium, from Group IB ions other than gold, from Group IIB ions other than mercury, and from ions of the lanthanides, and mixtures of these.

[0014] It is understood that the zeolite adsorbents of this invention are used in form of shaped particles also known as secondary particles. These secondary particles may be shaped by a series of methods into various geometrical forms such as, for example, beads, extrudates, etc. Beading, extruding and other shaping methods utilize inorganic materials as binders added to

the zeolitic crystalline phase prior to the shaping process. These binders allow for necessary mechanical strength of the particles and creation of a macropore system in the interior of the latter ones needed for effective sorption performance properties. The binder content may vary widely depending on the type of binder materials used, i.e., between about 5 and 25 weight % of the final product. Chemical composition of binders has not been taken into account where, in this invention, Si/Al elemental ratios are referred to. For this particular reason, the expression "Si/Al elemental ratio of the zeolitic phase" is being used throughout.

[0015] Binder types and shaping procedures as far as the adsorbent materials of the current invention are concerned, are well known and therefore need not be further described herein.

[0016] Typically, regeneration is carried out at a temperature sufficiently higher than the adsorption temperature of the process. Typical regeneration temperatures are in the range of 50 to about 300° C, preferably between the range of 100 to 250° C.

[0017] The novel TSA procedure of the present invention is directed to the use of the class of zeolitic adsorbent materials which have been identified as not only suitable for the removal of nitrogen oxides, in particular dinitrogen oxide, N₂O, but also of hydrocarbons from air. For this purpose, the novel adsorbent class comprises X-type zeolite with a Si/Al elemental ratio of the zeolitic phase that ranges from 0.9 to 1.3, whose exchangeable cations on an equivalent basis include about 0 to about 100 % calcium ions, and about 100 to about 0 % other ions, the other ions being selected from the group consisting of Group IA ions such as lithium, sodium and potassium, from Group IIA ions other than calcium, from Group IB ions other than gold, from Group IIB ions other than mercury, and from ions of the lanthanides, and mixtures of these, preferably, however, from 0.9 to 1.15, and a cation composition of this adsorbent comprises from about 60 to about 100 % of calcium ions and about 40 to about 0 % of cations being selected from the Group IA such as lithium, sodium and potassium, from Group IIA ions others than calcium, from Group IB ions others than gold, from Group IIB ions others mercury, and from ions of the lanthanides, and mixtures of these, and especially preferred between 0.95 and 1.05, and a cation composition that comprises from about 95 to about 100 % of calcium ions and about 5 to about 0 % of cations being selected from the group consisting of Group IA ions such as lithium, sodium and potassium, from Group IIA ions other than calcium, from Group IB ions other than gold, from Group IIB ions other than mercury, and from ions of the lanthanides, and mixtures of these. The materials with a Si/Al elemental ratio from 0.9 to 1.15, and the described cation compositions will here and further on be named as calcium Low-Silicon X-type zeolite (CaLSX type zeolite).

[0018] The method according to the invention is particularly suited to the removal from air of nitrous

oxide in addition to water vapour and carbon dioxide.

[0019] The advantage of the present invention resides in its relative simplicity. It has been discovered that by the use of a third adsorbent layer comprising CaLSX type zeolite that one can simply convert a temperature swing adsorption PPU unit into a unit which not only removes water and carbon dioxide from gas streams prior to entry into the cryogenic air separation unit, but also removes the undesirable nitrogen oxides, especially dinitrogen oxide, and saturated as well as non-saturated hydrocarbon gases present in the air stream. This leads to an air stream entering the cryogenic distillation unit which is substantially free of trace impurities such as water, carbon dioxide and also nitrogen oxides as well as hydrocarbons. This resultant highly purified air stream entering the cryogenic air separation unit results in a much safer plant and enables the air separation unit to give products which have an even higher purity than that previously attained.

[0020] In a typical example of a TSA process of the present invention air containing water, CO_2 and trace impurities comprising nitrogen oxides (e.g., N_2O , NO , etc.) and hydrocarbons (e.g., acetylene, propane, etc.) is passed into a PPU containing three separate layers of adsorbent material. The first layer which contacts the air stream comprises an adsorbent which removes substantially all of the water from the air. Typically, the first adsorbent may comprise activated alumina although other known water adsorbent sieve materials such as zeolite NaX may be utilized. The substantially water free air is then passed through a second adsorbent layer capable of removing substantially all of the CO_2 from the air stream. The second adsorbent layer comprises a zeolite X material, in particular a NaX-type zeolite where the Si/Al elemental ratio of the zeolitic phase ranges from 0.9 to 1.3. Finally, the air stream substantially free of H_2O and CO_2 passes through a third adsorbent layer comprising a Ca X-type zeolite wherein the Si/Al elemental ratio of the zeolitic phase ranges from 0.9 to 1.3 to remove substantially all of the nitrogen oxides and hydrocarbons impurities from the air. The resulting air stream exiting the TSA-PPU may then be fed directly into a cryogenic air separation unit for separation of the oxygen and nitrogen.

[0021] It is envisaged that CaX-type zeolites in the ranges of Si/Al ratio and cation compositions of this invention may also be utilized for trace removal such as removal of N_2O and saturated and unsaturated hydrocarbon gases from air in multi-layer pressure swing adsorption PPU systems, and/or in combined temperature swing/pressure swing adsorption systems.

[0022] Methods according to the present invention will now be described in the following examples with reference to the accompanying drawings, in which:

Fig. 1 is a graphical representation of sorption capacity ratio versus pressure for the $\text{N}_2\text{O}/\text{CaLSX}$ system over the $\text{N}_2\text{O}/\text{NaLSX}$ system for curve 1,

and the $\text{N}_2\text{O}/\text{CaLSX}$ system over the CO_2/NaLSX system for curve 2 (Example 2); and

Fig. 2 is a graphical representation of percent (%) retained of two impurities, C_2H_4 and N_2O , versus time for a 28 inch bed packed with CaLSX type zeolite adsorbent as described in Example 3.

Example 1:

10 (Comparative Example)

[0023] A feed air stream saturated with water and containing the following trace impurities was passed through a bed packed with 1.3 ft of Activated Alumina and 2 ft layer of a NaX type zeolite at pressure, $P = 71$ psia, and temperature, $T = 61$ °F:

$$\begin{aligned}\text{CO}_2 &= \sim 400 \text{ ppm} \\ \text{CH}_4 &= 2.2 \text{ ppm} \\ \text{N}_2\text{O} &= 0.3 - 0.35 \text{ ppm} \\ \text{C}_2\text{H}_2 &= 0.40 - 0.48 \text{ ppm} \\ \text{C}_2\text{H}_4 &= 1.4 - 1.6 \text{ ppm} \\ \text{C}_2\text{H}_6 &= 1.4 \text{ ppm} \\ \text{C}_3\text{H}_6 &= 0.55 - 0.75 \text{ ppm} \\ \text{C}_3\text{H}_8 &= 1.5 - 1.6 \text{ ppm} \\ \text{n-C}_4\text{H}_{10} &= 1.6 - 1.8 \text{ ppm}\end{aligned}$$

[0024] Prior to CO_2 breakthrough from the adsorbent bed the following trace impurities completely break through in the sequence : CH_4 , C_2H_6 , C_3H_8 , N_2O and C_2H_4 . This implies that these impurities will end up in the cryogenic plant in their entirety and this could cause an unsafe operation.

35 EXAMPLE 2:

[0025] Sorption Isotherms for systems CO_2 / NaLSX, N_2O / NaLSX and N_2O / CaLSX (all beads with c. 12 wt. % of binder) for a temperature, $T = 298.15$, were evaluated from sorption isotherms measured directly as concentration dependences, by means of an isosteric sorption technique with minimum dead volume the principle of which is described in the paper, D. Shen and M. Bülow, *Microporous and Mesoporous Materials*, 22 (1998) 237-249. The elemental Si/Al ratio of the CaLSX material amounted to 1.05, and its calcium cation exchange value was about 99%. These isotherms are shown in a half-logarithm scale, in Fig. 1 of this example. The half-logarithm scale is chosen to show more clearly the differences in sorption behaviour for the three systems, which are exhibited especially in their low-pressure isotherm regions. The specific sorption behaviour in these regions is responsible for trace removal in PPU processes. Fig. 1 teaches that at sorption equilibrium gas pressures, < 0.5 torr, the sorption capacity of CaLSX for N_2O exceeds significantly that of NaLSX for CO_2 . The preferred sorption strength in the N_2O / CaLSX system, as compared with that feature for

the two other systems holds for very broad temperature regions, especially within the region. (0 to 100) °C. This makes the CaLSX zeolite a preferred N₂O selective sorbent to remove a few ppm N₂O from air in front of ASUs.

EXAMPLE 3:

[0026] A feed air stream saturated with water and containing the above mentioned trace impurities was passed through a bed packed with a 28 inch packed bed of a CaLSX type zeolite adsorbent, available as Siliporite G586, bead size 1.6 to 2.5 mm, from CECA of France, at pressure, P = 71 psia, and temperature, T = 61 °F. Prior to CO₂ breaking through the adsorbent bed, the following trace impurities break completely through in the sequence: CH₄, C₂H₆, and C₃H₈. Most noteworthy is that neither N₂O nor C₂H₄ break through the column prior to the CO₂ breakthrough. Since TSA-PPU bed design is based upon CO₂ breakthrough, this implies that no traces of these impurities will enter the cryogenic plant which results in a safe operation of these plants. By employing a deeper bed of CaLSX, other impurities, notably C₃H₈, can be removed.

Claims

1. A process for the removal of impurities from a gas stream by thermal swing adsorption comprising sequentially passing said gas stream through a first adsorbent layer which removes water from said gas stream, a second adsorbent layer comprising an NaX zeolite thereby removing CO₂ from said gas stream, and a third adsorbent layer comprising an X zeolite wherein the second and third adsorbents have a Si/Al elemental ratio of the zeolitic phase between 0.9 to 1.3, with a cation composition of the third layer adsorbent, on an equivalent basis, that comprises about 0 to about 100 % calcium ions, and about 100 to about 0 % other ions, the other ions being selected from the group consisting of Group IA ions, from Group IIA ions other than calcium, from Group IB ions other than gold, from Group IIB ions other than mercury, and from ions of the lanthanides, and mixtures of these thereby removing nitrogen oxide(s) and hydrocarbon(s) from said gas stream.

2. A process as claimed in claim 1, wherein said first adsorbent layer is activated alumina.

3. A process as claimed in claim 1, or claim 2 wherein said second adsorbent layer is a sodium X zeolite having a Si/Al elemental ratio of the zeolitic phase between 0.9 and 1.3.

4. A process as claimed in claim 3, wherein said second adsorbent layer is a sodium X zeolite having a

Si/Al elemental ratio of the zeolitic phase between 0.9 and 1.15.

5. A process as claimed in claim 4 wherein said second adsorbent layer is a sodium Low-Silicon X zeolite having a Si/Al elemental ratio of the zeolitic phase between 0.95 and 1.05.

6. A process as claimed in any one of the preceding claims wherein said third adsorbent layer is a X zeolite having a Si/Al elemental ratio of the zeolitic phase between 0.9 and 1.15.

7. A process as claimed in any one of the preceding claims, wherein said third adsorbent layer is a calcium Low-Silicon X zeolite having a Si/Al elemental ratio of the zeolitic phase between 0.95 and 1.05 and a cation composition that comprises from about 95 to about 100 % of calcium ions and about 5 to about 0 % of cations being selected from the group consisting of Group IA ions, from Group IIA ions other than calcium, from Group IB ions other than gold, from Group IIB ions other than mercury, and from ions of the lanthanides, and mixtures of these.

8. The process as claimed in any one of the preceding claims, wherein said Group IA ions are selected from the group consisting of lithium, sodium and potassium.

9. A process as claimed in any one of the preceding claims wherein said gas stream comprises air and said nitrogen oxide comprises N₂O.

10. A process as claimed in any one of the preceding claims, wherein said hydrocarbon is ethylene.

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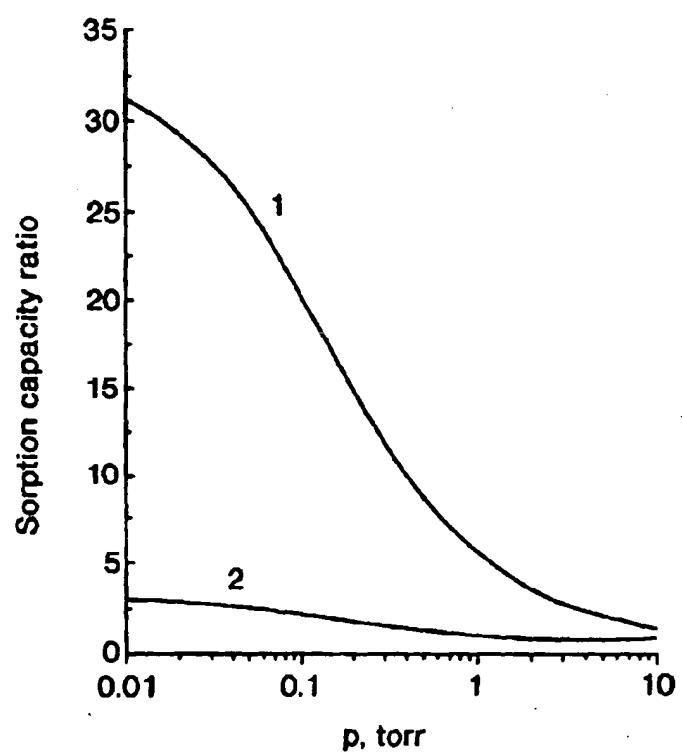


FIG. 1

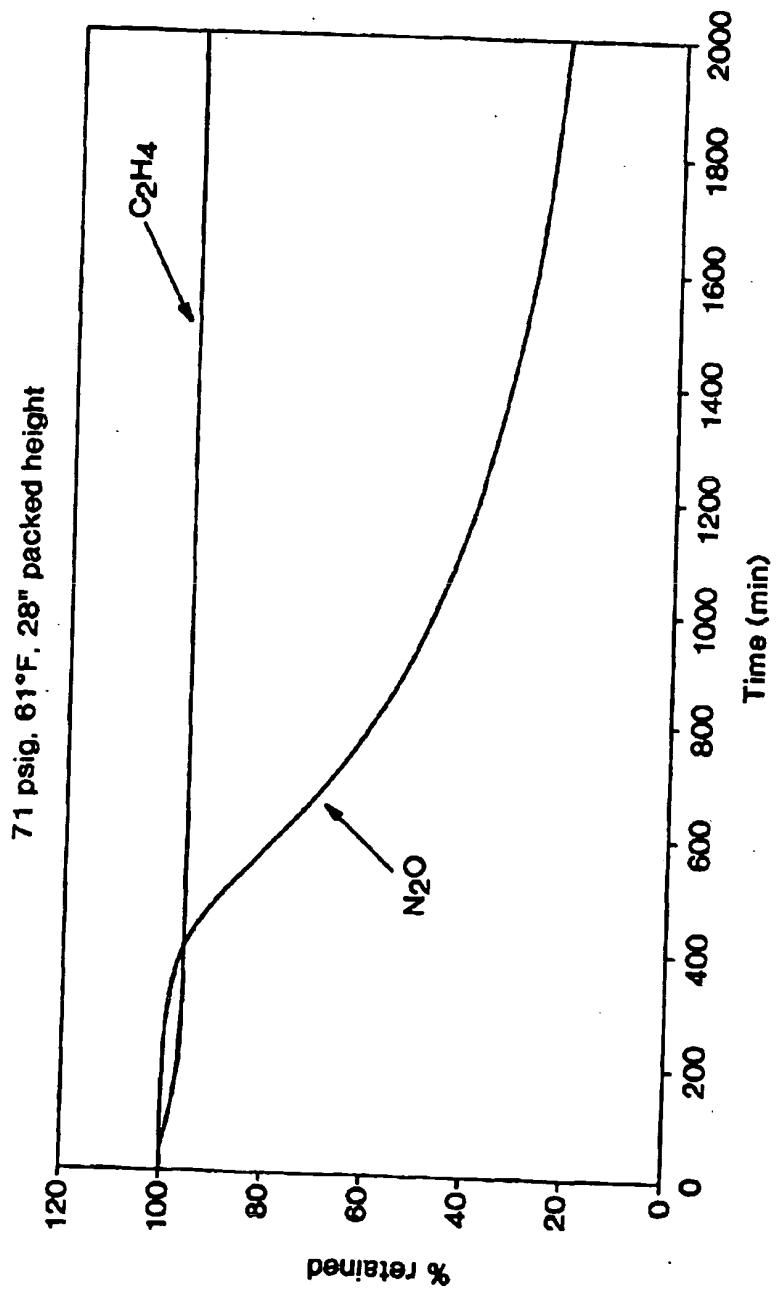


FIG. 2